Two Poly(2,5-thienythiazolothiazole)s: Observation of Spontaneous Ordering in Thin Films†

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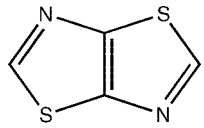
ABSTRACT: The synthesis and properties of two new polymers based on thiazolothiazole are described. The polymers dissolve in common organic solvents such as chloroform and chlorobenzene. Their molecular weights are in the kDa range with polydispersities on the order of 1.1−1.3 as determined by GPC. The X-ray crystal structure of one monomer was determined. Interplanar $\pi-\pi$ interaction and short S···N contacts (3.20 Å) were observed in the crystal. The monomers and polymers strongly fluoresce in solution. Their quantum yields range from 23 to 55% relative to 9,10-diphenylanthracene and rhodamine B. Contrary to expected polymer behavior, the polymers are unusual in that they self-assemble upon drop-casting. The thin films of polymers exhibited sharp reflection peaks in the low-angle region in XRD measurement, indicating a highly ordered assembly.

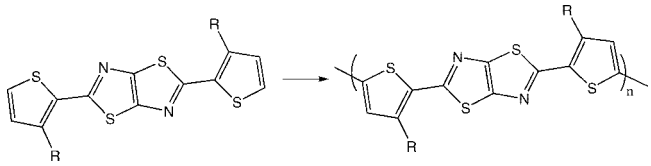
Introduction

In 2006, McCullough et al. obtained very high mobility results with a poly(thienothiophene-*co*-alkyldithiophene).[1] The polymer is a hole conductor in FET devices. As is well-known, organic electronics is dominated by materials that are hole-transporters. Electron-transporting materials are more rare. The thienothiophene core can also be considered as a better electron donor than acceptor and hence would give rise to hole-transporting polymers. On the other hand, thiazolothiazole (see TzTz, below), due to its C═N bonds is expected to be considerably more electronegative than thienothiophene, yet should have approximately the same shape.



Thiazolothiazole
TzTz

In fact, TzTz is not unknown to the organic electronics community. Yamashita[2] has prepared n-channel FETs with excellent properties, and TzTz was incorporated, albeit in small amounts, as a copolymer with polyfluorene.[3] Much more recently, it was a ter-monomer in a copolymer with fluorene and poly(3-hexylthiophene) (P-3HT).[4] In an effort to improve on existing n-channel semiconductor devices based on conjugated polymers, we designed, synthesized, and evaluated the photophysics and electrochemistry of the novel copolymers TzTz-*co*-diAT depicted below. We also determined the solid-state structure of the corresponding monomers.



Monomers and polymers of alternating TzTz and alkyl dithiophene. R = hexyl and decyl.

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The synthesis of the monomers and polymers is shown in Scheme 1[7] and is based on the original work on the preparation of the parent system.[5] The condensation of dithiooxamide with the respective aldehydes to produce the monomers proceeded in only very moderate yield, as did the oxidative polymerization in chloroform. The latter could be improved to better yields in hot chlorobenzene.[6]

Physical Properties

The monomers are crystalline, yellow solids, soluble in a number of common organic solvents. They are stable to the atmosphere at ambient temperature over a period of several months. The polymers are colored powders that are also soluble in common organic solvents, except methanol and other very polar media.

The molecular weight of the polymers was determined using gel permeation chromatography (GPC), MALDI-TOF, and light scattering. The molecular weight of the polymers does not depend on either of the two preparation methods. The GPC in THF showed for the hexyl-substituted polymer a M_w of 2305 g/mol and polydispersity of 1.08. For the decyl-substituted polymer a M_w of 2082 g/mol and polydispersity of 1.29 while MALDI-TOF showed 1893 and 1421 for the hexyl and 2344 and 1758 for the decyl—clearly very modest values. However, their typical polymer behavior (viscosity, film formation) made these values suspicious. Much higher M_w values were recorded with light-scattering measurements that gave $M_w = 1.33 \times 10^6$ g/mol for the hexyl-substituted polymer and $M_w = 4.32 \times 10^6$ g/mol for the decyl-substituted polymer. These values were reproducible (see Supporting Information for the raw data reports). As a control, we also measured the light scattering of rr-poly(3-hexylthiophene) whose GPC molecular weight was determined to be ca. 7000 g/mol, and the molecular weight from light scattering was found to be 1.72×10^4 g/mol. It would appear that GPC is in agreement with MALDI regarding order of magnitude, and light scattering overestimates the molecular weight by more than 1 order of magnitude.

The thermal properties of the monomers were investigated by differential scanning calorimetry (DSC), **4a** has a sharp melting peak at 73.8 °C and what appears to be a broad crystallization peak, more akin to a glass transition between 55 and 35 °C (Figure 1). Monomer **4b** shows a sharp melting peak at 72.92 °C. A very broad "crystallization" peak was observed between 40 and 70 °C (Figure 2). The monomers were also quite thermally stable (see Supporting Information) as determined by thermogravi-

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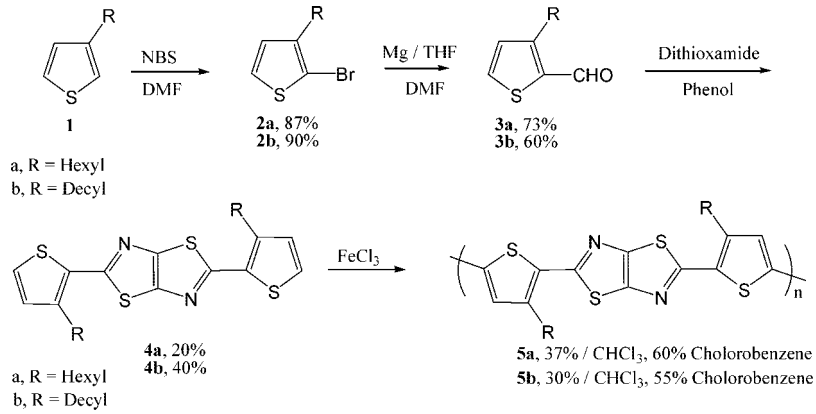
Scheme 1



metric analysis (TGA). Polymers **5a** and **5b** were found to exhibit very good thermal stability, losing less than 5% of their weight on heating to about 400 °C (Figures 3 and 4).

Electronic Spectroscopy

The monomers are slightly yellow and the polymers deep red. Monomers and polymers are also fluorescent materials (monomers, blue; polymers, red-orange; Figures 5 and 6). The relative quantum yields for fluorescence were measured in chloroform solution relative to 9,10-diphenylanthracene and rhodamine B for the monomers and polymers, respectively. Monomers **4a** and **4b** exhibited a quantum yield of 0.55 and 0.23, respectively, and polymers **5a** and **5b** of 0.27 and 0.40, respectively. Whereas the absorption spectra did not exhibit vibronic structure, the emission spectra showed two bands and a longer wavelength shoulder in both cases (monomer and polymer). Also, the polymer absorption and emission were red-shifted by ca. 100 nm relative to the monomers.

Electrochemistry

Figures 7 and 8 show the cyclic voltammetry of monomers **4a** and **4b**, respectively. It is clear that all processes are irreversible. As expected and due to the electron-deficient properties of thiazolothiazole, these monomers exhibited a reduction peak at accessible negative potentials. Attempts to obtain a reversible process by varying the usual parameters, especially scan rate, proved unsuccessful.

The polymers also showed irreversible processes as depicted in Figures 9 and 10. Their reduction potentials reflect better electron-accepting properties by ca. 0.5 eV than those of the corresponding monomers. These results may not augur well for

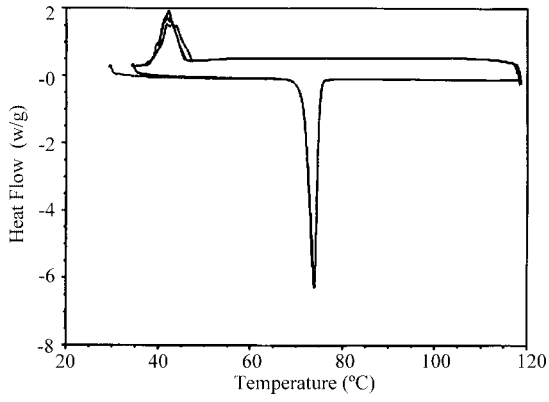


Figure 1. DSC thermogram of monomer **4a**. Heating rate at 5 °C/min; cooling rate at 5 °C/min.

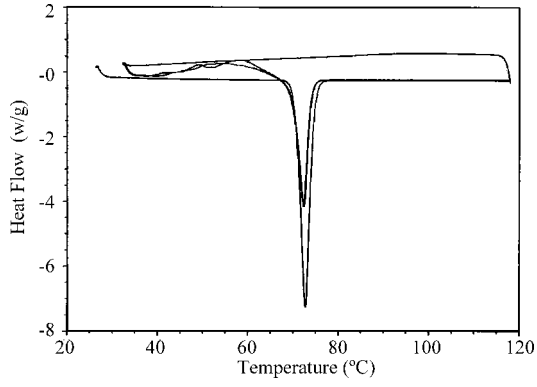


Figure 2. DSC thermogram of monomer **4b**. Heating rate at 5 °C/min; cooling rate 5 °C/min.

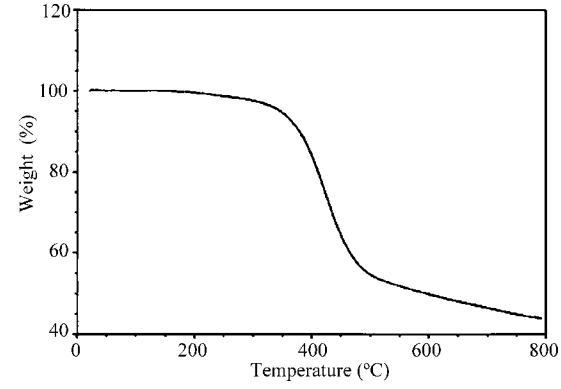


Figure 3. TGA curve of polymer **5a**. Heating rate at 10 °C/min; wt = 2.0 mg.

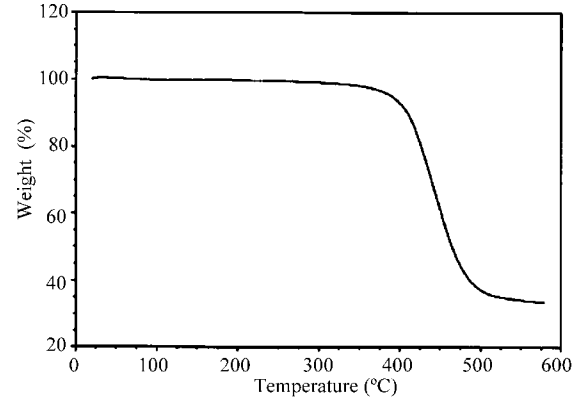


Figure 4. TGA of polymer **5b**. Heating rate at 10 °C/min; wt = 4.05 mg.

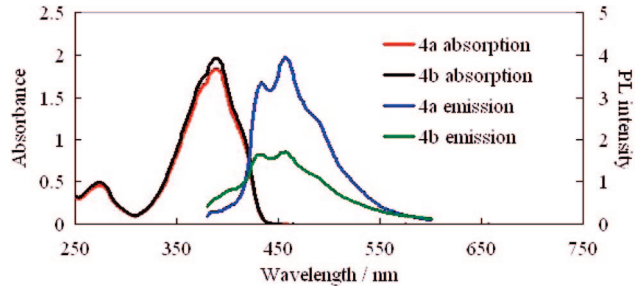


Figure 5. UV−vis absorption and PL emission spectra of monomers in chloroform.

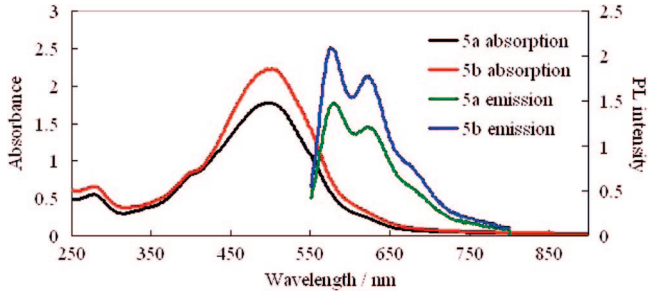


Figure 6. UV−vis absorption and PL emission spectra of polymers in chloroform.

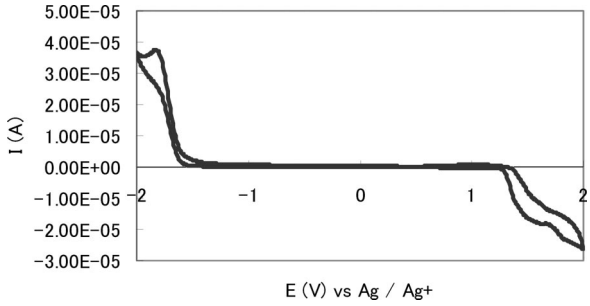


Figure 7. CV of monomer **4a** in 0.1 M Bu_4NClO_4/CH_2Cl_2 at a scan rate of 50 mV/s. The first oxidation potential at 1.50 V; the reduction potential at −1.87 V vs Ag/Ag^+ ($E_{1/2\ ferrocene}$ = 0.60 V in the same solution).

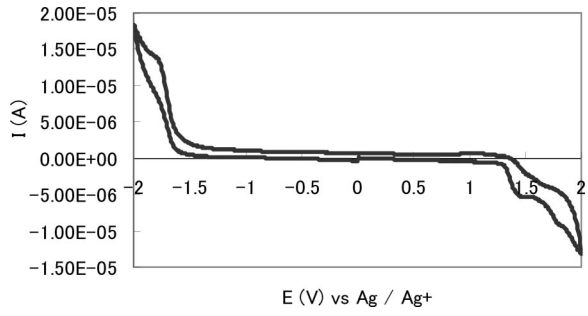


Figure 8. CV of monomer **4b** in 0.1 M Bu_4NClO_4/CH_2Cl_2 at a scan rate of 50 mV/s. The first oxidation potential at 1.46 V; the reduction potential at −1.81 V vs Ag/Ag^+ ($E_{1/2\ ferrocene}$ = 0.58 V in the same solution).

device performance. The LUMO levels of polymer **5a** and **5b** were 4.00 and 4.02 eV, respectively, and were calculated from their oxidation potentials and optical gaps. These values are close to the compounds which showed n-type FET properties in their devices.[2a] These results indicate that these materials are candidates for n-type materials.

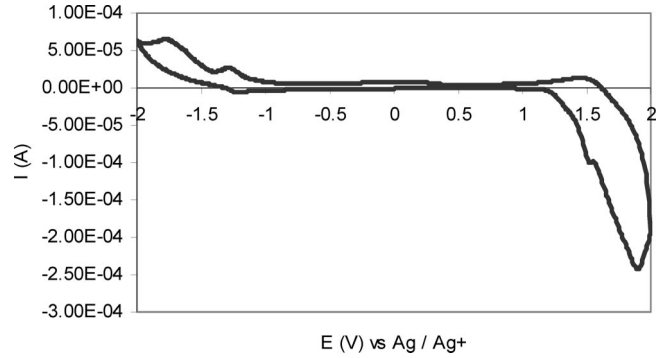


Figure 9. CV of polymer **5a** thin film in 0.1 M Bu_4NClO_4/acetonitrile at a scan rate of 50 mV/s. The first oxidation potential at 1.55 V; the reduction potential at −1.32 V vs Ag/Ag^+ ($E_{1/2\ ferrocene}$ = 0.61 V in the same solution).

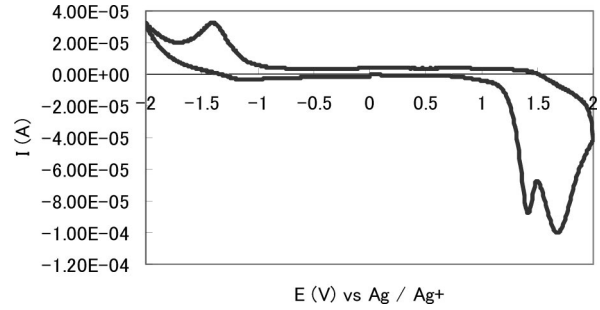


Figure 10. CV of polymer **5b** thin film in 0.1 M Bu_4NClO_4/acetonitrile at a scan rate of 50 mV/s. The oxidation potential at 1.43 V; the reduction potential at −1.44 vs Ag/Ag^+ ($E_{1/2\ ferrocene}$ = 0.63 V in the same solution).

X-ray Structure

Figure 11 shows the face to face π-stacking in the crystal structure of **4a** with an interplanar separation of 3.47 Å. Also, a 3.20 Å short S···N interaction was found in this crystal structure (see Tables 1 and 2). It is significantly shorter than the sum of the corresponding van der Waals radii (3.35 Å). An unusual feature of this structure is the non-coplanar disposition of the side chains.

These systems have the unusual feature to order upon thin-film formation. The structural ordering of these monomers and polymers in thin films was studied by X-ray diffraction (XRD) and is shown in Figure 12. Thin films were prepared on a SiO_2 surface by drop-casting from chlorobenzene, followed by annealing at 60 °C for 1 h. The thin films of monomer **4a** and **4b** displayed high crystallinity, with strong primary diffraction peaks at 2θ = 6.52° and 4.90°, corresponding to d spacing of 13.0 and 18.0 Å.

Polymer **5b** exhibits sharp reflection peaks in the low-angle region. The first peak at 16.50 Å, indexed as a (100) reflection, can be assigned to the interchain spacing between the two polymer main chains, which are segregated by the alkyl substituents. A second-order reflection is also clearly observed, implying a highly ordered assembly of the polymer molecules (see Figures 12 and 13). On the other hand, the thin film of the hexyl-substituted polymer (**5a**) showed poor crystallinity compared to the decyl-substituted polymer. This can be attributed to more disorder of the hexyl-derived polymer on the SiO_2 substrate.

Conclusion

We have synthesized two new monomers and two polymers containing the thiazolothiazole unit. These monomers and polymers exhibited strong fluorescence in solution and irrevers-

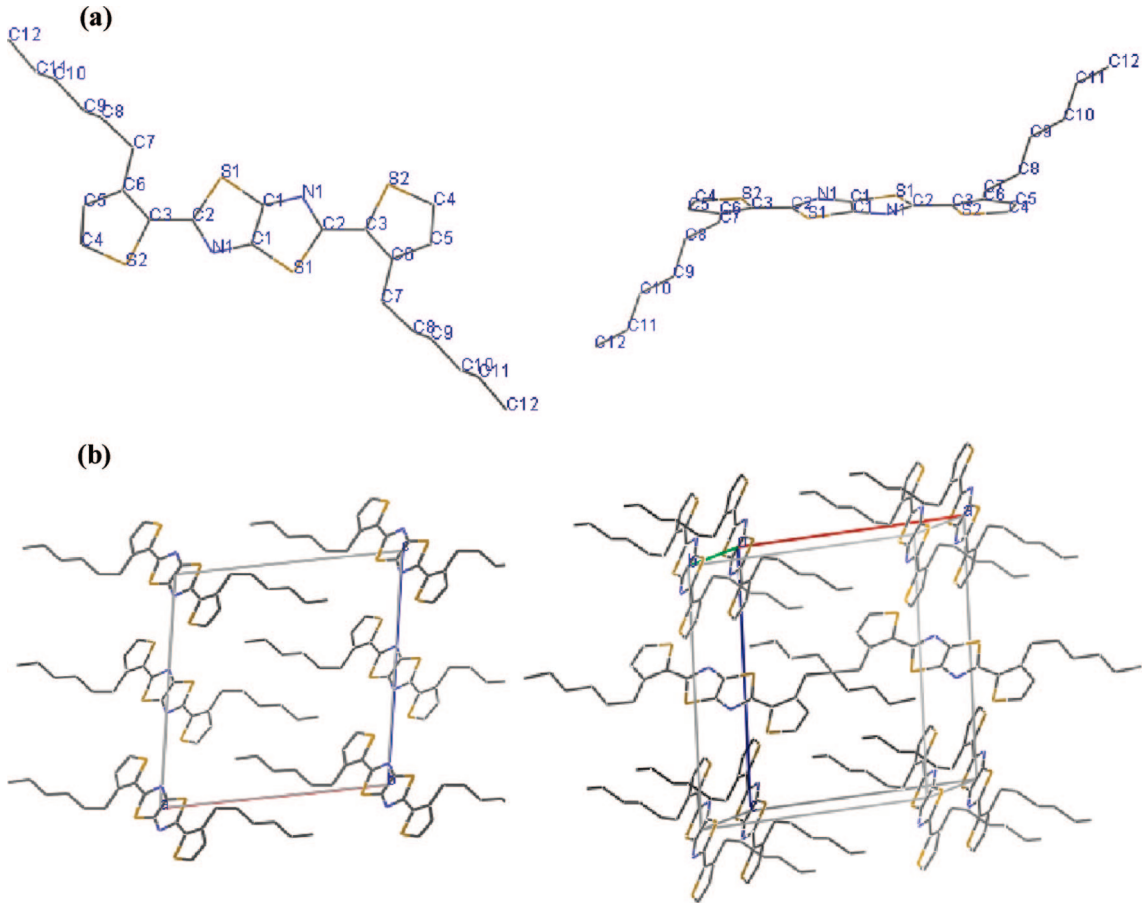


Figure 11. Crystal structure of compound **4a**: (a) top view and side view of the molecule; (b) molecular packing.

Table 1. Bond Lengths (Å) and Angles (deg) for 4a[a]

C(1)−N(1)#1	1.349(4)	N(1)#1−C(1)−C(1)#1	119.1(4)
C(1)−C(1)#1	1.377(6)	N(1)#1−C(1)−S(1)	132.7(2)
C(1)−S(1)	1.724(3)	C(1)#1−C(1)−S(1)	108.1(3)
C(2)−N(1)	1.315(4)	N(1)−C(2)−C(3)	121.7(3)
C(2)−C(3)	1.452(5)	N(1)−C(2)−S(1)	115.3(2)
C(2)−S(1)	1.762(3)	C(3)−C(2)−S(1)	123.0(3)
C(3)−C(6)	1.370(5)	C(6)−C(3)−C(2)	131.9(3)
C(3)−S(2)	1.731(3)	C(6)−C(3)−S(2)	112.2(3)
C(4)−C(5)	1.341(5)	C(2)−C(3)−S(2)	115.8(3)
C(4)−S(2)	1.705(4)	C(5)−C(4)−S(2)	111.8(3)
C(5)−C(6)	1.418(5)	C(4)−C(5)−C(6)	114.6(4)
C(6)−C(7)	1.506(5)	C(3)−C(6)−C(5)	110.2(3)
C(7)−C(8)	1.491(6)	C(3)−C(6)−C(7)	125.5(3)
C(8)−C(9)	1.460(7)	C(5)−C(6)−C(7)	124.2(3)
C(9)−C(10)	1.496(6)	C(8)−C(7)−C(6)	117.4(3)
C(10)−C(11)	1.445(7)	C(9)−C(8)−C(7)	119.6(4)
C(11)−C(12)	1.481(7)	C(8)−C(9)−C(10)	117.8(4)
N(1)−C(1)#1	1.349(4)	C(11)−C(10)−C(9)	119.3(5)
		C(10)−C(11)−C(12)	116.7(5)
		C(2)−N(1)−C(1)#	108.6(3)
		C(1)−S(1)−C(2)	88.80(15)
		C(4)−S(2)−C(3)	91.05(18)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+2, -y-1, -z+1$.

ible to quasi-reversible oxidation peaks in cyclic voltammetry experimetns. In the X-ray diffraction (XRD) spectra, the thin films of these monomers and polymers exhibited sharp reflection peaks in the low-angle region, indicating a highly ordered assembly of monomers and polymers. The fabrication of FET devices is currently underway.

Experimental Section

General Information. ^{1}H NMR spectra were recorded on a Varian Unity Inova 400 MHz spectrometer with TMS as the internal standard and $CDCl_3$ as solvent. Mass spectral analysis (MS) were performed on a VG70 Magnetic Sector Instrument system. Melting points were measured using a Mel-Temp 2 device and were uncorrected. UV−vis−NIR spectroscopy was performed on an Agilent UV−vis spectrophotometer. TGA and DSC were determined on a TA Instruments Q50 and Q10, respectively. The single-crystal structures were obtained from a Bruker 3-axis platform diffractometer equipped with a 2.4 kW Mo tube as X-ray source. A Scintag X2 $\theta-\theta$ diffractometer was used in thin-film X-ray diffraction (XRD) measurements. Cyclic voltammetric measurements were carried out on a Princeton Applied Research potentiostat/galvanostat model 263A with a three-electrode cell, with 0.1 M Bu_4NClO_4 (tetrabutylammonium perchlorate) in anhydrous CH_2Cl_2or acetonitrile. A Ag/Ag^+ electrode, a platinum wire, and a sealed platinum rod were used as the reference, counter, and working electrode, respectively.

2-Bromo-3-hexylthiophene (2a). NBS (*N*-bromosuccinimide) (5.29 g, 0.029 mol) was dissolved in 25 mL of DMF. This mixture was added dropwise to a solution of 3-hexthylthiophene (5.0 g, 0.029 mol) in DMF (30 mL) in the dark. This solution was stirred at room temperature overnight and was poured into 100 mL of water. The aqueous layer was extracted with ethyl ether (3 × 50 mL), and the organic extracts were washed with water, followed by brine and dried over anhydrous $MgSO_4$. After removal of solvents, the remaining organic liquid was chromatographed on silica gel (hexane) to give 6.45 g of compound **1a**, yield 87%. ^{1}H NMR: (δ) 7.11 (d, 1H), 6.92 (d, 1H), 2.60 (t, 2H), 1.72−1.44 (m, 3H), 1.44−1.20 (m, 5H), 0.98 (m, 3H).

3-Hexylthiophene-2-carboxaldehyde (3a). To a round-bottom flask equipped with a condenser, 2-bromo-3-hexylthiophene (2.18 g, 8.86 mmol) and a catalytic amount of iodine were added to a dry THF (25 mL) suspension of Mg turnings (0.22 g, 9.16 mol) under a constant stream of argon. The mixture was allowed to stir vigorously and was heated to reflux for 5 h; the solution was

Table 2. Intermolecular Short Distance of 4a

atom 1	atom 2	distance (Å)
C7	S1	3.169
C7	S1	3.169
N1	S2	3.203
S2	N1	3.203
S2	N1	3.203
N1	S2	3.203
C5	C9	3.405
C5	C9	3.405
C6	C1	3.471
C1	C6	3.471
C6	C1	3.471
C1	C6	3.471
C2	C2	3.519
C2	C2	3.519
N1	C4	3.546
C4	N1	3.546
C4	N1	3.546
N1	C4	3.546
C5	C2	3.586
C2	C5	3.586
C2	C5	3.586
C5	C2	3.586
C4	N1	3.598
N1	C4	3.598
N1	C4	3.598
C4	N1	3.598
N1	C5	3.69
N1	C5	3.69
C5	N1	3.69
C5	N1	3.69
S2	C4	3.7
C4	S2	3.7
C4	S2	3.7
S2	C4	3.7

cannulated to a previously dried flask. Anhydrous DMF (1.2 mL) was added dropwise to this solution at room temperature, and the mixture was allowed to stir overnight. The reaction was quenched with 100 mL of 5% HCl, and THF was removed on a rotary evaporator. The aqueous layer was extracted with ether (3 × 5 mL). The organic layer was washed with saturated sodium bicarbonate and water, followed by drying over $MgSO_4$. After the removal of solvents, the crude was chromatographed on silica gel (5% ethyl acetate in hexane) to give **2a**: 1.28 g, yield 73%. ^{1}H NMR: (δ) 10.05 (s, 1H), 7.66 (d, 1H), 7.03 (d, 1H), 2.98 (t, 2H), 1.67−1.43 (m, 3H), 1.30−1.11 (m, 5H), 0.89 (m, 3H).

2,5-Bis(3-hexylthiophen-2-yl)-thiazolo[5,4-*d*]thiazole (4a). Dithiooxamide (0.70 g, 5.85 mmol), 2 g of phenol, and **3a** (2.30 g, 11.7 mmol) were combined in a round-bottom flask and were heated in an oil bath at refluxing temperature for 45 min. The crude product was purified by column chromatography on silica gel (5% ethyl acetate in hexane) to give **4a**: 0.54 g, yield 20%. ^{1}H NMR: δ 7.38 (d, 2H), 7.02 (d, 2H), 3.02 (t, 4H), 1.80−1.61 (m, 6H), 1.57−1.22 (m, 10H), 0.98−0.91 (m, 5H). MS/EI: 474 (M^+).

Poly-2,5-bis(3-hexylthiophen-2-yl)-thiazolo[5,4-*d*]thiazole (5a). *Chloroform Method.* A solution of **4a** (0.35 g, 0.74 mmol) in 5 mL of chloroform was added to dried $FeCl_3$ (0.47 g, 2.9 mmol) in 10 mL of chloroform in a round-bottom flask under an argon atmosphere. The solution turned black immediately upon addition and was allowed to stir at room temperature for 48 h. The resulting mixture was poured into 200 mL of methanol, followed by stirring at room temperature for 1 h. The resulting precipitate was filtered and then added to a well-stirred mixture of methanol (200 mL) and aqueous ammonia (50 mL). The suspension was stirred at room temperature for 12 h. After filtration, the solid was purified in a Soxhlet extractor with methanol for 24 h. The remaining solid residue was extracted with 200 mL of chloroform overnight. Removal of solvent form the extract gave 0.13 g of dark green polymer product (37%). ^{1}H NMR: (δ) 7.01 (d, 2H), 2.95 (br, 4H), 1.95−1.80 (br, 6H), 1.78−1.10 (br, 10H), 1.02−0.91 (br, 5H).

Chlorobenzene Method. A solution of **4a** (0.30 g, 0.63 mmol) in 5 mL of chlorobenzene was added dropwise to a 5 mL of chlorobenzene solution containing dried $FeCl_3$ (0.51 g, 3.1 mmol) in a round-bottom flask under an argon atmosphere. The solution turned black immediately after addition. This mixture was heated to 60 °C and maintained at this temperature for 48 h. Upon cooling to room temperature, the mixture was poured into 200 mL of

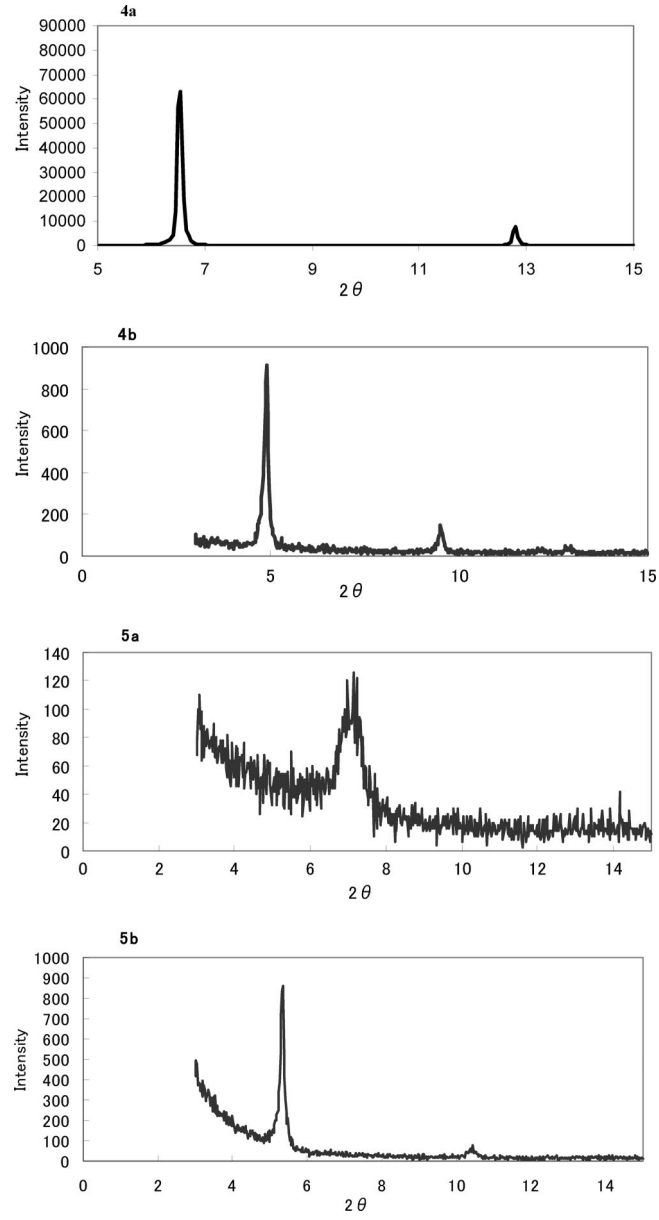


Figure 12. X-ray diffraction of drop-cast thin films of monomers **4a**, **5a** and polymers **4b**, **5b**.

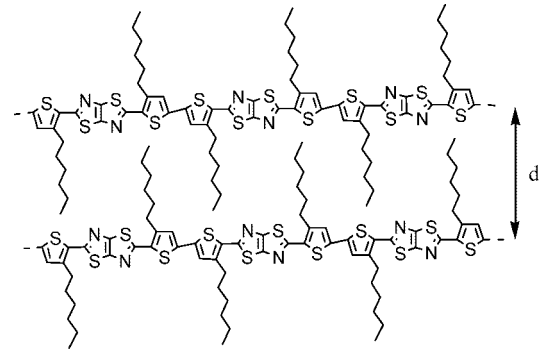


Figure 13. Schematic representation of arrangement of two polymer chains for **5a** and **5b**.

methanol and allowed to stir at room temperature for 1 h. The precipitate was filtered and added to a well-stirred mixture of methanol (200 mL) and aqueous ammonia (50 mL) and allowed to stir at room temperature for 12 h. After filtration, the solid was extracted with methanol in a Soxhlet extractor for 24 h. The remaining solid residue was extracted with 200 mL of chlorobenzene overnight. Evaporation of the extract gave 0.18 g of dark green polymer product (60%).

The decyl compounds were prepared by the same method as the hexyl compounds. Characterization specifics are given below.

2-Bromo-3-decylthiophene (2b). Yield 90%. ^{1}H NMR: δ 7.20 (d, 1H), 6.80 (d, 1H), 2.68 (t, 2H), 1.70−1.18 (m, 16H), 0.95 (m, 3H).

3-Decylthiophene-2-carboxaldehyde (3b). Yield 60%. ^{1}H NMR: δ 10.04 (s 1H) 7.65 (d, 1H), 7.01 (d, 1H), 2.98 (t, 2H), 1.68−1.26 (m, 16H), 0.88 (m, 3H).

2,5-Bis(3-decyl-thiophen-2-yl)-thiazolo[5,4-*d*]thiazole (4b). Yield 40%. ^{1}H NMR: δ 7.37 (d, 2H), 7.01 (d, 2H), 3.01 (t, 4H), 1.72−1.27 (m, 32H), 0.88 (m, 6H).

Poly-2,5-bis(3-decyl-thiophen-2-yl)-thiazolo[5,4-*d*]thiazole (5b). *Chloroform Method.* Yield 30%. ^{1}H NMR: δ 7.01 (br, 2H), 2.99 (br, 4H), 1.80−1.10 (br, 32H), 0.90 (br, 6H).

Chlorobenzene Method. Yield 55%.

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Supporting Information Available: Crystal data tables and light scattering raw data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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